

**ANALYSIS OF THE
AUTOMATE "YELLOW 96" PROCESS
USING
REACTION CALORIMETRY**

**TO : U.S. Chemical Safety &
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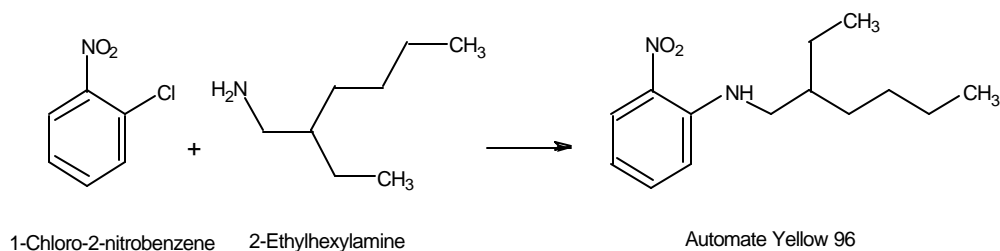
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INTRODUCTION

Initial correspondence between Mr. David Heller from the U.S. Chemical Safety & Hazard Investigation Board (USCSHIB) in Washington, DC, and Mr. Richard Wedlich of Chilworth Technology, Inc. focused around a report review of an incident that took place in Paterson, NJ. The site of the incident was the Morton plant during the synthesis of a dye product – Automate “Yellow 96”.

It was determined that further thermal analysis should be conducted on the synthesis process. Several different experiments were suggested on the reactants, the process, and the final product. The aim of this particular study is to produce calorimetric information for the synthesis process following the manufacturing conditions (the initial charge of 2-ethylhexylamine and the reaction as it carries out over three sequential heat steps). The Mettler RC-1 reaction calorimeter is used to evaluate the reaction conditions.

N-(2-ethylhexyl)-2-nitrobenzenamine, a.k.a. Automate Yellow 96 is prepared by aminating 1-chloro-2-nitrobenzene with 2-ethylhexylamine at elevated temperatures. Due to the fact that the starting materials and products are liquids at the desired reaction temperatures the reaction is run neat, without solvent.



REFERENCES

Morton International, Inc., Paterson Plant Incident – April 8, 1998,
“Report of the Incident Investigation Committee,” April 12, 1998.

Draft of 1/11/00 U.S. Chemical Safety and Hazard Investigation Board,
Investigation Report, Chemical Manufacturing Incident (9 Injured),
Morton International, Inc., Paterson, NJ April 8, 1998,
Report No. 1998-06-I-NJ

RESULTS

Table I is the summary of results from the reagent addition and heat step to initiate the reaction (calorimetric processes) run in the RC-1.

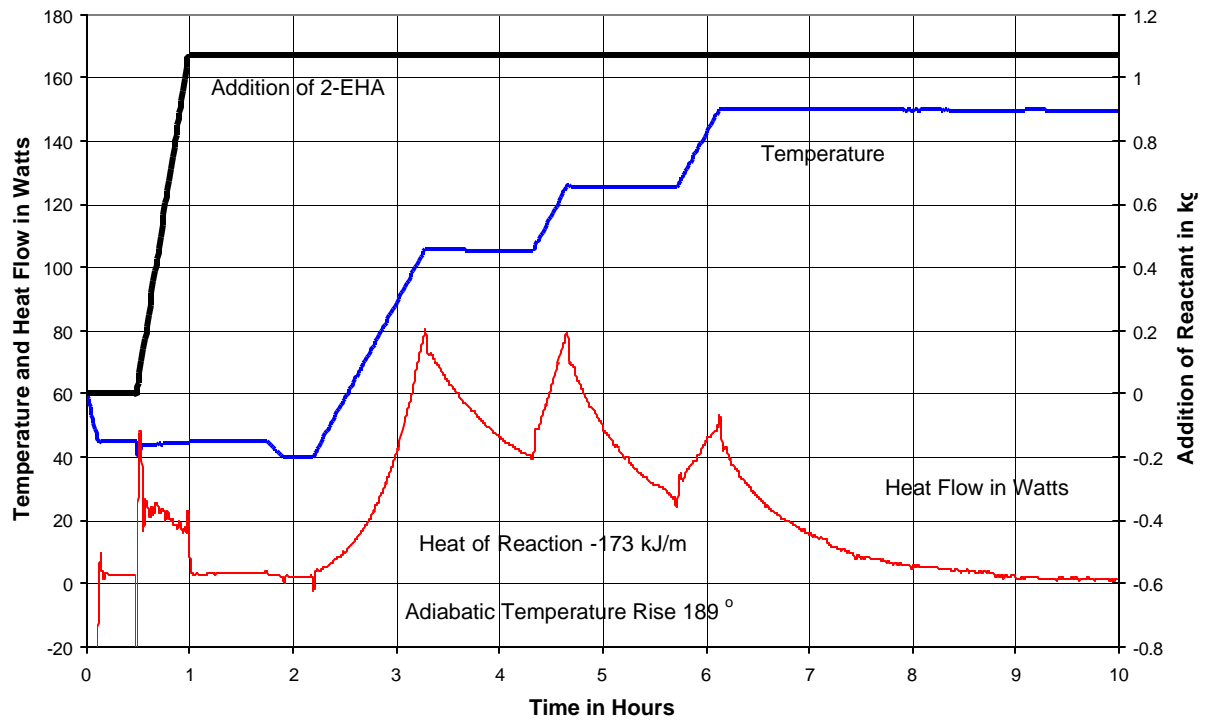
Table I: Results of RC-1 Testing

Step	Temperature (°C)		Mass (kg)	Heat Capacity Cp (J/kg K)	D H (kJ/mol)	D T _{AD} (°C)	Process Summary
1	45	45	.654	2045.3	- 6.9	8.2	Addition of 2-EHA to o-NCB
2	40	105	1.724	2047.7	- 70.4	78.9	First Heat Step of Reaction
3	105	125	1.724	2149.0	- 57.2	60.7	Second Heat Step of Reaction
4	125	150	1.724	2204.0	- 45.6	49.9	Third Heat Step of Reaction
5	40	150	1.724	2045.3 (40° C) 2200.0 (150° C)	- 173.2	189.5	Total Reaction 45° C to 150° C

Legend:

ΔH = Heat of Reaction per Mol of NCB

ΔT_{AD} = Adiabatic Temperature Rise if Cooling or Heating Stops

Graph #1**RC1, U.S. Chemical Safety Board, Automate Yellow 96**

CONCLUSIONS

Addition of 2-Ethylhexylamine to 1-Chloro-2-nitrobenzene

The addition of 2-ethylhexyl amine to 1-chloro-2-nitrobenzene at 45° produced an immediate rate controlled exothermic response; which ended, as the addition was complete. This addition had a heat of reaction of -6.9 KJ/mol with an adiabatic temperature rise of 8.2° C. It is impossible to determine from this experiment if this response is due to heat of mixing or heat of reaction.

40° C to 105° C Heating Ramp and 1 Hour 105° C Heating Period

As the reaction is heated from 40° C to 105° C over 65 minutes the reaction produces an immediate exothermic response, which builds to a maximum heat output of 80 watts as the reaction temperature approaches 105° C. As the reaction is maintained at 105° C the heat flow decreases but does not completely end leaving a large amount of accumulated energy for the next step. This process step had a heat of reaction of -70.4 KJ/mol with an adiabatic temperature rise of 78.9° C.

105° C to 125° C Heating Ramp and 125° C Heating Period

As this reaction was heated to 125° C over 20 minutes the reaction, again, produced an exothermic response; which reached a maximum heat output of about 80 watts as the reaction temperature approached 125° C. As the reaction was maintained at 125° C for one hour the heat flow decreased but did not end, leaving a large amount of accumulated energy for the next step. This process step had a heat of reaction of -57.2 KJ/mol with an adiabatic temperature rise of 60.7° C.

125° C to 150° C Heating Ramp and Four Hour Period

As the reaction was heated from 125° C to 150° C over 25 minutes the reaction once again produced an exothermic response; which reached a maximum rate of about 53 watts as the reaction temperature reached 150° C. By the end of the four-hour heating period the heat flow decreased to zero indicating that the reaction was over.

Overall reaction

When the above three heating periods are combined, the heat of reaction becomes - 173.2 kJ/mole with an adiabatic temperature rise of 189.5° C. It is clear that if this process were run in a reactor without adequate cooling the reaction could easily self-heat into a temperature range where the product could begin to decompose.

EXPERIMENTAL SECTION**Test Objective:**

The objectives of this experiment were:

- To observe the addition of the 2-ethylhexylamine for noticeable exothermic behavior.
- To determine the heat of reaction associated with the synthesis process over the three heat steps.
- To determine the adiabatic temperature rise associated with the synthesis process over the three heat steps.

Full details of the testing rational and RC-1 reaction calorimetry techniques are provided in **APPENDIX B & C**, respectively.

Materials:

1-Chloro-2-nitrobenzene	654g	$(654\text{g} / 157.6 \text{ g/mol} = 4.15 \text{ mol})$	Aldrich
2-Ethylhexylamine	1070g	$(1070\text{g} / 129.3 \text{ g/mol} = 8.27 \text{ mol})$	Aldrich

Equipment:

Mettler RC1 with RD10 Controller (See diagram in **APPENDIX A**)

AP01 (1.8 Liter glass reactor)

Standard Stainless Steel Reactor Head

Metering Pump, Balance

File Names US2713.CSV

Method:

A complete and formal process description was provided by the client. The client also forwarded two reports (Morton & U.S. Chemical Safety and Hazards Investigation Board) that described the synthesis process in great detail as well as background information concerning the process.

The experimental process used to investigate the synthesis of **Automate Yellow 96** in the RC-1 calorimeter can be divided into two major parts. The two major steps of the evaluation were; the addition of the 2-ethylhexylamine and the heat steps applied to the sample to initiate the reaction.

2-Ethylhexylamine Addition

The solid 1-chloro-2-nitrobenzene (654 g) was charged to the glass RC-1 reactor and warmed to form a liquid. The speed of the glass anchor stirrer was adjusted to 120 rpm and a calibration was performed. After settling the 2-ethylhexylamine (1070 g) was added to the reactor (via pump) over 30 minutes, at 45° C. After the last of the 2-EHA was charged to the reactor, the mixture was allowed time to settle. Ten minutes after the contents of the reactor were stabilized; a 10-minute calibration was performed. The temperature was ramped down from 45° C to 40° C over 10 minutes to determine a heat capacity. After settling, another 10-minute calibration was performed.

Heating Periods

To avoid rapid overheating (which may lead to runaway conditions), the reaction mixture was heated in three steps. Heat was applied to the system; the reaction was initiated, and allowed a wait period to continue reacting. This procedure was followed for each of the heat steps with an increase in temperature allowing more and more of the reactants to interact.

The reaction mixture was heated from 40° C to 105° C over 65 minutes, and held at 105° C for 60 minutes. The reaction temperature was then increased to 125° C over 20 minutes and held at 125° C for 60 minutes. The final heating step raised the reaction temperature to 150° C over 25 minutes. This reaction temperature was maintained for 4 hours, and during this four-hour period, three 10-minute calibrations were performed. The temperature was ramped back down to 45° C in a manner which facilitated heat capacities and calibrations to be taken at all of the temperatures that were significant in the temperature ramp of the first portion of the synthesis process.

APPENDIX A

APPENDIX B : TESTING RATIONAL

Reaction Calorimetry

Reaction calorimetry is used to characterize the synthesis process under normal conditions. Specifically, the process is run in the calorimeter and a determination of: the heat capacity, heat transfer coefficient, and heat of reaction is made. The heat capacity and heat of reaction data are used to estimate the adiabatic temperature rise from the process (i.e. the temperature rise that will occur if the forced process cooling or heating fails). An estimation is made of the maximum attainable temperature reached by the synthesis process if loss of cooling occurs. This temperature can be compared to the onset temperature for thermal decomposition of the reactants, intermediates and products (as determined in screening/adiabatic calorimetry tests). The comparison is used to assess the likelihood of a secondary decomposition leading to a thermal runaway in the event of loss of cooling.

APPENDIX C : HEAT FLOW CALORIMETRY

The principle of heat flow calorimetry is based on measuring the quantity of heat that flows across the reactor walls as an exothermic or endothermic process takes place. The total heat flow across the reactor wall is proportional to the temperature difference between the reaction mass contents and the reactor jacket.

This can be written mathematically as:

$$Q_f = UA(\Delta T_{LM})$$

Where:

Q_f	=	heat Flow	(W)
U	=	Overall heat transfer coefficient	(W/m ² /K)
A	=	Heat exchange area	(m ²)
ΔT_{LM}	=	Log mean temperature difference given by (($T_r - T_{j1}$) - ($T_r - T_{j2}$))/Ln(($T_r - T_{j1}$)/($T_r - T_{j2}$)) and approximates to ($T_r - T_j$)	(K)
T_r	=	Temperature of the reaction mass	(°C)
T_j	=	Temperature of the heat exchange medium	(°C)

The constant of proportionality (UA) is determined by electrical calibration of the reactor contents before and after the reaction.

The heat released or absorbed by any reaction occurring in the reactor at any period in time can be directly determined by performing a heat balance across the system. The heat flow due to the reaction is made up of the measured heat flow across the reactor wall, the heat supplied or removed by dosing of reagents, the heat accumulated in the reaction mass and the heat lost to the surroundings.

$$Q_r = Q_f + Q_d + Q_a + Q_l$$

Where:

Q_r	= Reaction heat flow
Q_f	= Measured heat flow
Q_d	= Heat flow through dosing
Q_a	= Accumulated heat
Q_l	= Heat losses

The heat flow due to dosing, Q_d , is the product of: the rate of dosing of reagent, the specific heat capacity of the dosed reagent, and the temperature difference between the reaction mass and the dosed reagent.

The accumulated in the reaction mass, Q_a , is the product of the rate of the change of reaction mass temperature, the mass of the reactor contents and the specific heat capacity of the contents.

By measuring Q_f , Q_d , and Q_a ; a figure for the enthalpy change occurring in the calorimeter during the reaction can be determined. By performing electrical calibrations both before and after the reaction, the change in heat transfer areas and the environmental heat losses, Q_l , can be accounted for. The heat flow calorimeter employed in this assessment operates in such a manner as to keep the reaction mixture at a desired test temperature until the procedure dictates that the temperature of reaction conditions be modified.

The calorimeter consists of four separate modules:

- i) A jacketed, agitated reaction vessel in which the reaction (under study) is performed.
- ii) A thermostatically controlled heat transfer medium which is pumped around the jacket vessel.
- iii) An electric calibration heater and associated regulated power supply.
- iv) A temperature monitoring system.

Determination of the reaction enthalpy change in a reaction system employing a heat flow calorimeter is undertaken in three distinct phases.

These are:

- i) Initial calibration phase.
- ii) Reaction phase.
- iii) Final calibration phase

The system under investigation is examined in a semi-batch operation. The reaction solvent and starting materials are charged to calorimeter and allowed to reach equilibrium with the jacket temperature. Upon reaching equilibrium, the calibration heater is activated and a known quantity of electrical energy is input to the system. This will cause the temperature of the reactor contents to rise slightly; triggering the jacket heat transfer fluid temperature to decrease until a dynamic equilibrium is established. The rate of heat removal by the heat transfer medium and environmental heat losses will equal to the rate of heat supplied by the heater.

When the calibration heater is switched off, the jacket temperature will revert to equilibrium with the reaction mass temperature. The integral of the power differential with time (in Watt-seconds) can be expressed directly to the total quantity of electrical energy supplied by the calibration heater. This ratio is directly proportional to the overall heat transfer coefficient and the heat transfer area. The value determined here will necessarily incorporate a factor for the total environmental heat loss.

Once the first calibration has been completed and the reaction mass temperature is once again in equilibrium with the jacket, the reaction phase is started. The reagent is added to the vessel at a constant rate using the peristaltic pump and the reaction mass temperature and jacket temperature monitored. If during the reagent addition and exothermic process takes place the reaction mass temperature will change. Providing the process is exothermic, the temperature of the oil will decrease until dynamic equilibrium is achieved whereby the rate of heat evolution in the reacting system matches the sum of the rate of heat removal by the jacket and environmental losses (under near isothermal conditions). The converse occurs if the reaction is endothermic. Once the addition is complete, the jacket oil temperature is allowed to revert to temperature equilibrium with the sample.

The time taken for temperature equilibration to re-establish itself is dependent on the rate of reaction. If the reaction rate is fast, or essentially instantaneous, equilibrium with the jacket temperature will be achieved rapidly. However, if the rate of reaction is slow the jacket temperature will be achieved rapidly. However, if the rate of reaction is slow and some unreacted reagent accumulation occurs in the vessel, then there will be a considerable “work-off” period following completion of the addition before temperature equilibrium is re-established. The quantity of accumulated heat is determined as a percentage of the overall heat release.

Once this has been achieved, a second calibration is undertaken. Note that integration of the temperature-time trace will give a UA value that is different to the data from the first calibration since the active heat transfer area has changed and the physical properties of the reaction mixture may have changed.

By comparing the two electrical calibrations with measured heat release due to the reaction, the heat of reaction is determined. The calorimeter can be operated in isothermal or iso-peribolic mode. The performance of temperature ramps can be used to determine the heat capacity of the reaction mass. A full review of the operation and uses of the calorimeter can be found in a paper by Regenas, W., American Chemical Society Symposium Series No. 65, 1979, pp37-49. The equipment is represented diagrammatically in **APPENDIX A -Figure 1**.

APPENDIX D

US Chemical Safety Board
"Yellow 96"

